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Integration of nano-Al with Co_3O_4 nanorods to realize high-exothermic core–shell nanoenergetic materials on a silicon substrate

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ABSTRACT

Nanoenergetic materials (*n*EMs) have better performance in ignition and energy release rate compared to conventional energetic materials. This makes them have promising applications in actuation, ignition, propulsion, power, fluidic, and electro-explosive devices at the micro and nanoscale. In this study, Co_3O_4 is used for the first time to achieve novel Al/Co_3O_4 based *n*EMs by integrating nano-Al with Co_3O_4 nanorods that are synthesized by a chemical method. The total heat of reaction, especially the exothermic reaction before Al melting, is greatly enhanced by using Co_3O_4 pure nanostructures (no microscale film exits). The *n*EMs are fabricated onto a silicon substrate, which is very convenient to achieve promising functional nanoenergetics-on-a-chip. The fabricated *n*EMs are confirmed to have nanoscale mixing, very high heat of reaction, and significantly reduced onset temperature of the major exothermic reaction by scanning electron microscopy, differential thermal/thermogravimetric analysis, and differential scanning calorimetry.

1. Introduction

Energetic materials including propellants, explosives and pyrotechnics have found various defense and civilian applications [1]. Nanoenergetic materials (*n*EMs) are proved to have better performance in ignition and energy release rate than conventional energetic materials due to the larger contact area and shorter diffusion distance of fuel and oxidizer. Therefore, *n*EMs represent a new frontier for energetic material research [2–5]. Many methods have been introduced to synthesize *n*EMs including physical mixing, sol–gel, sputtering of multilayer foils, integration of Fe_2O_3 nanowires with an Al film, aero-gel, integration of oxidizers with porous silicon, molecular self-assembly, and others [6–32]. Each method has its own merits. However, many of the aforementioned methods suffer from certain shortcomings. For instance, physical mixing presents some limitations such as not homogeneous distribution of oxidizer and fuel leading to large scatter in their ignition and burning characteristics, and poor compatibility with microsystem. In sol–gel, the random distribution of the particles and the inherent organic impurities result in limited performance. Aero-gel is not currently suitable for mass production. Therefore, it is desirable to develop novel, facile and also scalable methods to synthesize *n*EMs with nanoscale mixing and homogeneity.

Recently, Al/CuO based *n*EMs have been made by integrating nano-Al (by thermal evaporation or magnetron sputtering) with one-dimensional CuO nanowires grown from Cu thin film to form core/shell structures with CuO nanowires as the core and Al as the shell [17,29]. This approach has the advantages of improved mixing uniformity, enhanced contact, reduced impurities and Al oxidation, and lower activation energy [17,29]. Moreover, one very promising direction in *n*EMs research is to integrate *n*EMs with silicon-based microelectromechanical systems (MEMS) to achieve functional nanoenergetics-on-a-chip (NoC) because NoC is the key for many applications of *n*EMs such as actuation, ignition, propulsion, power, fluidic, and electro-explosive devices at the micro and nanoscale [2,11,19,21–22,30]. In order to achieve NoC, Zhang et al. [17] synthesized Al/CuO nanowires based *n*EMs onto silicon, a basic material for microelectronics and MEMS. And then they developed a functional nanoinitiator by integrating the Al/CuO based *n*EMs with a Au/Pt/Cr microheater fabricated onto a substrate [21], where the *n*EMs are successfully ignited by the microheater through joule heating. The work in [17] opens the door to achieve NoC; but the nanostructure (CuO nanowires) is only a very small portion of the entire structure whereas a big portion of the structure is in the form of microscale thin film that lays underneath the CuO nanowires (see Fig. 2 in [17]) as shown schematically in Fig. 1a. The Al is not contacting much of the film, which reduces very much the reaction rate and heat of reaction of the *n*EMs. Similar problem also exists in the CuO/Al core/shell based *n*EMs [29]. There is a 2 μm thick CuO thin film layer beneath the CuO nanowires. The CuO thin film layer was found

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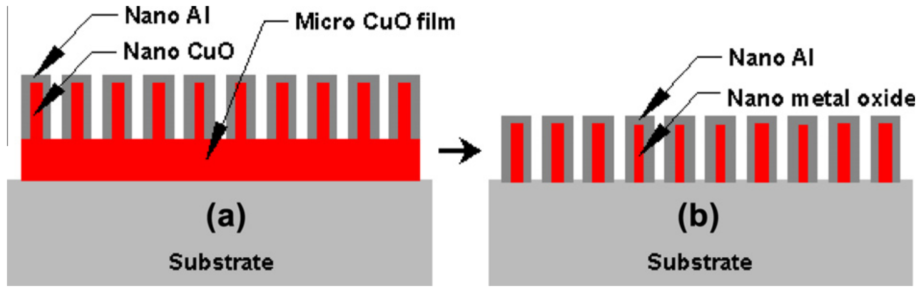

Fig. 1. Sketch of *n*EMs composed of: (a) nanofuel and nano/microscale oxidizer, and (b) nanofuel and nanooxidizer (no microscale oxidizer).

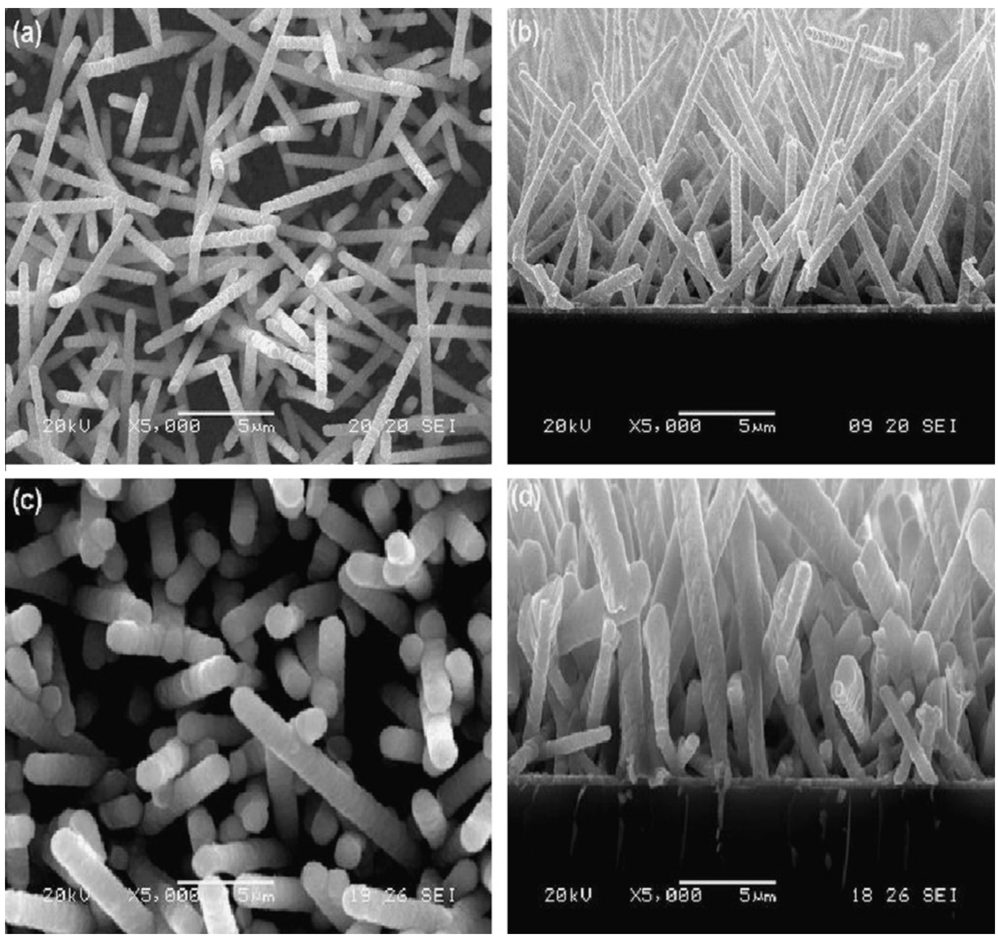

Fig. 2. SEM images of the Co_3O_4 nanorods: (a) top view and (b) cross-section view; SEM images of the Al/Co_3O_4 *n*EMs: (c) top view and (d) cross-section view.

to react with Al at higher temperature compared to CuO nanowires, which leads to the broadening of the heat release profile. The microscale CuO layer always exists if the CuO nanowires are synthesized by the thermal oxidation of copper foil and/or film. This is a feature that cannot be dealt with by varying synthesis parameters [17,29]. Altering the synthesis methodology may be a way to remove the microscale CuO layer. But no report is found in the literature to synthesize vertically aligned CuO nanowires without microscale CuO.

It is desirable to have some *n*EMs composed of pure nanofuel and oxidizer (no microscale fuel and oxidizer exit) as shown schematically in Fig. 1b, which are expected to have improved performance. Furthermore, many kinds of metal oxides (Fe_2O_3, CuO, CuO_x, $KMnO_4$, MoO_3, NiO, WO_3, Bi_2O_3, etc.) have been used to combine/integrate with Al to realize Al/metal-oxide based *n*EMs [6–9,12–19,21,23–30]. However, there is no report in the literature to study the Al/Co_3O_4 based *n*EMs although the combination of Al and Co_3O_4 is promising thermite since the reaction between Al and Co_3O_4 shown in Eq. (1) has a high theoretical heat of reaction of 4232 J/g and adiabatic reaction temperature of 3201 K [33].

$$8Al + 3Co_3O_4 \rightarrow 4Al_2O_3 + 9Co \tag{1}$$

In this study, Al/Co_3O_4 based *n*EMs are synthesized by integrating nano-Al with Co_3O_4 nanorods that are synthesized through a chemical route. The heat of reaction, especially the exothermic reaction before Al melting, is greatly increased by using Co_3O_4 pure nanostructures (no microscale film exits). The *n*EMs are fabricated onto a silicon substrate, which is very convenient to achieve promising functional NoC. The fabricated *n*EMs are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), differential thermal/thermogravimetric analysis (DTA–TG), and differential scanning calorimetry (DSC).